

## Superconductivity Centennial Conference

The irreversibility line and Curie-Weiss temperature of the superconductor  $\text{LaCaBaCu}_{3-x}(\text{BO}_3)_x$  with  $x=0.2$  and  $0.3$ L. De Los Santos Valladares<sup>a,b,\*</sup>, A. Bustamante Dominguez<sup>c</sup>, R. Bellido Quispe<sup>c</sup>,  
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**Abstract**

$\text{LaCaBaCu}_3\text{O}_7$  is a high critical temperature superconductor (HTS) below the  $T_c = 80$  K and its structure is similar to that of YBCO. In this work we study the effect in the irreversibility line and the Curie-Weiss temperature of this superconductor after borate  $(\text{BO}_3)^{3-}$  doping ( $\text{LaCaBaCu}_{3-x}(\text{BO}_3)_x\text{O}_{7-\delta}$   $x=0.2$  and  $0.3$ ). Interestingly, borate doping enhances the irreversibility line and this effect is probably caused from alteration the arrangement of the oxygen atoms in the crystalline structure. Moreover, the Curie-Weiss temperature ( $\chi_p$ ) in the normal state increases with doping concentration. Calculated  $\chi_p$  for pure  $\text{LaCaBaCu}_3\text{O}_7$  is around -98K, this value increases to -75 and 49 K for  $x=0.2$  and  $0.3$  respectively and indicating transition from antiferromagnetic to ferromagnetic coupling between ions in the structure. This study provides additional data for the magnetic characteristics of doped like-123 crystalline structures with oxyanions.

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**Keywords:**  $\text{LaCaBaCu}_3\text{O}_7$ ; High Temperature Superconductor; Irreversibility line in superconductors, Curie-Weiss temperature.

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**1. Introduction**

It has been observed that the position of the irreversibility line ( $H_{irr}$ ) in the magnetic field vs temperature plot  $H(T)$  of high critical temperature superconductors (HTS) depends on different factors

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such as dimensionality, c-axis coupling strength and structural defects. For example, in Tl-2223 and Tl-1223, the  $H_{irr}$  line can be enhanced by producing columnar defects by heavy ion irradiation, [1]. This has also been observed in  $YBa_2Cu_3O_{7-\delta}$  (YBCO), after irradiation with 5 GeV Pb ions, columnar defects are produced in its structure and  $H_{irr}$  is enhanced [2, 3]. Crystallographic point defects (e.g oxygen vacancies) or Cu-O plane defects have been also suggested to alter the  $H_{irr}$  more effectively [1].  $LaCaBaCu_3O_7$  (La1113) is a HTS below the onset critical temperature  $T_{C(Onset)}=80$  K. Despite its crystalline structure is similar to YBCO [4, 5], not much research has been done in this HTS. In a previous works, we studied some magnetic and structural properties of La1113 and compared it to YBCO [6, 7]. In this work we study the effect of borate doing  $(BO_3)^{3-}$  in the  $H_{irr}$  and Curie-Weiss temperature ( $\square_p$ ) in this compound.

## 2. Experimental

Appropriate amounts of  $La_2O_3$ ,  $BaCO_3$ ,  $CuO$  and  $H_3BO_3$  were mixed and grinded to form pellets followed by calcinations at  $950^\circ C$  for 24h. The samples were reground and sintered at  $975^\circ C$  for 12 h before furnace cooling to room temperature (RT). After grinding for a third time, the samples were annealed at  $575^\circ C$  in  $O_2$  for 24 h and furnace cooled to RT in the same gas atmosphere. The final samples consisted on a powder sample of  $LaCaBaCu_{3-x}(BO_3)_xO_7$  with  $x=0.2$  and  $0.3$ . These powder samples prevent anisotropy conditions during measurements of their magnetic properties (i.e controlling the direction of the applied magnetic field to avoid screening induced currents was not necessary [8]). The magnetic measurements were performed in a DC Magnetic Property Measurement System (DC-MPMS-SQUID) from Quantum Design. The data were collected in Zero Field Cooling (ZFC) and Field Cooling (FC) modes in the field range of 100 Oe to 10 kOe and at different temperatures (10 - 290 K).

## 3. Results and discussions

The onset  $T_{C(Onset)}$ 's, calculated from the  $M(T)$  measurements (Figures 1 (a) and (b)), are 76 K and 73K for  $x=0.2$  and  $0.3$  respectively. The irreversibility temperatures ( $T_{irr}$ 's) were determined from each point at which the ZFC and FC  $M(T)$  loops separate. Thus, under the external applied magnetic field of 4 kOe  $M(T)$  measurements, like in the figures,  $T_{irr}$  are 56 K and 52K for  $x=0.2$  and  $0.3$  respectively. In general, multiple  $T_{irr}$  values from  $M(T)$  measurements obtained at many different applied field defined the irreversibility lines which are discussed next.

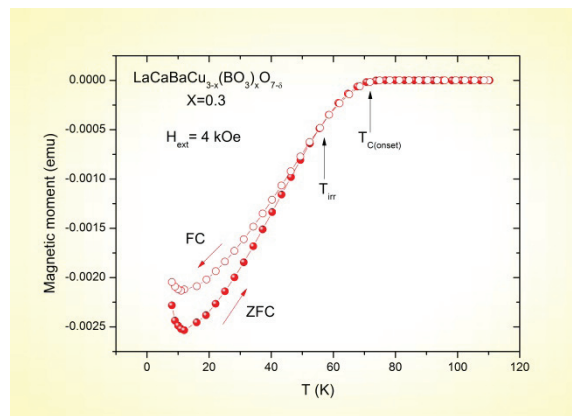
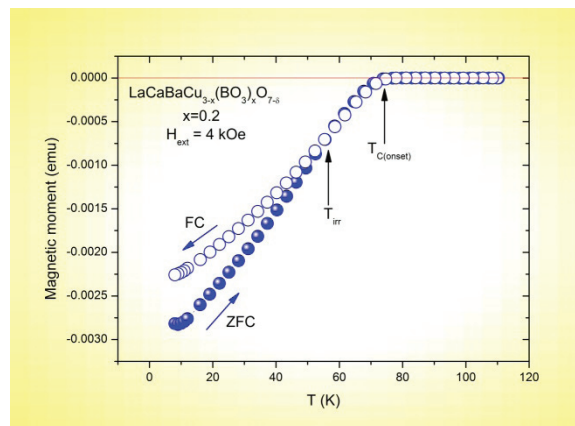
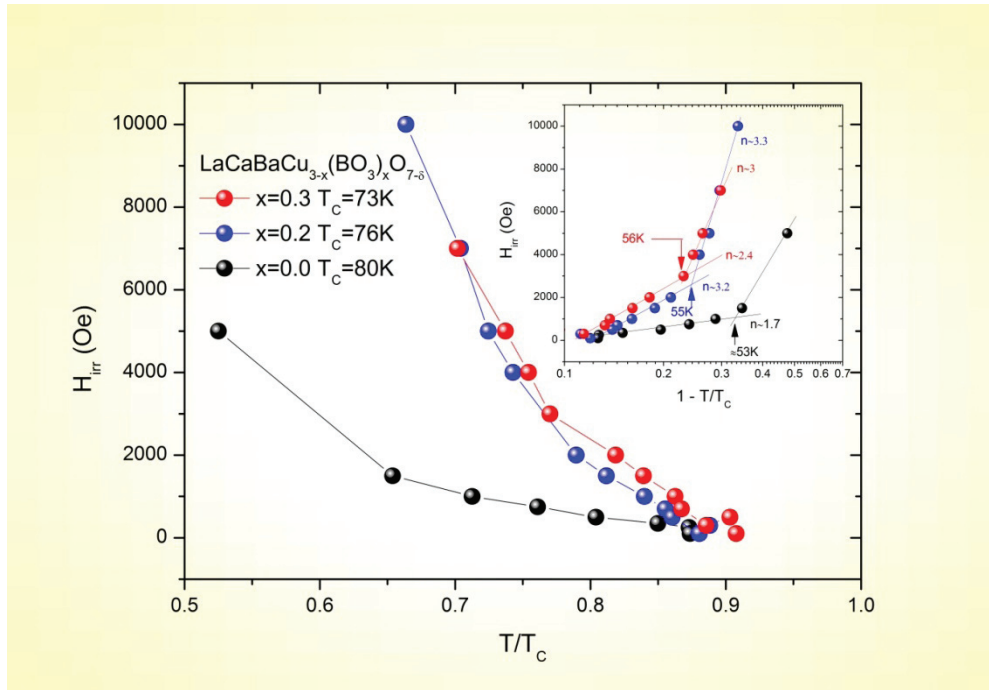


Fig. 1. Magnetic moment measurements as function of temperature ( $M(T)$ ) for  $\text{LaCaBaCu}_{3-x}(\text{BO}_3)_x\text{O}_{7-\delta}$  with  $x=0.2$  (left) and  $0.3$  (right). The irreversibility temperatures ( $T_{\text{irr}}$ ) are obtained from the points at which the ZFC and FC loops separate

The irreversibility lines for  $\text{LaCaBaCu}_{3-x}(\text{BO}_3)_x\text{O}_{7-\delta}$   $x=0.2$  and  $0.3$  are plotted in Figure 2. Notoriously, the irreversibility line of the  $\text{La1113}$  is enhanced when doping with borate. In contrast, it has been reported in other structures like in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  that  $H_{\text{irr}}$  shifts to lower values when  $\delta$  decreases [9]. In the present system, stoichiometric  $\delta$  decreases as  $x$  increases, thus, this effect could be related by the rearrangement of the oxygen atoms in the structure after the inclusion of  $(\text{BO}_3)^{3-}$ . In fact, inclusion of oxyanions like  $(\text{BO}_3)^{3-}$  or  $(\text{PO}_4)^{3-}$  in the  $\text{La1113}$  structure, produce the oxygen atoms in the charge reservoirs to rearrange, the cell parameters to change which in turn decreases the carrier density of the superconducting  $\text{CuO}_2$  planes and thus the  $T_C$  to decrease [10 - 12].  $H_{\text{irr}}$  fits the traditional trend proposed by Almasan et al [13] very well:

$$H_{\text{irr}} = H_{\text{irr}(0)} \left[ 1 - \frac{T}{T_C} \right]^n \quad (1)$$

Where  $H_{\text{irr}(0)}$  is time independent,  $T_C$  is the critical temperature (onset in our case) and the factor  $n$  provides an indication for applications of the superconductor (it varies considerably in different HTS [14]). In the case of YBCO, for  $n \approx 1.5$ , the irreversibility line is dominated by the “giant-flux creep” model [15, 16], whereas, for  $n \approx 2$ , the irreversibility line is dominated by the “flux-line melting” model [17, 18]. In this work, the  $n$  values obtained after fitting the  $H_{\text{irr}}(T)$  with two potential functions are shown inset in the figure. Changes in slope of each curve occur around 53, 55 and 55 K for  $x=0.0$ ,  $0.2$  and  $0.3$  respectively. In the undoped case ( $x = 0.0$ ),  $n \approx 1.7$ , this value is close to that for YBCO (1.5). However, after doing,  $n$  changes to values higher than 2, thus  $H_{\text{irr}}$  might be dominated by the flux-line melting model. Then enhance of  $H_{\text{irr}}$  line might be produced from the softening of the elastic parameters of the vortex system which make the pinning sites more effective.



**Figure 2.** Irreversibility lines for the  $\text{LaCaBaCu}_{3-x}(\text{BO}_3)_x\text{O}_{7-\delta}$  with  $x=0, 0.2$  and  $0.3$ .

Figure 3 shows the susceptibility dependence with the temperature  $\chi(T)$  of the  $\text{LaCaBaCu}_{3-x}(\text{BO}_3)_x\text{O}_{7-\delta}$  with  $x=0.2$  and  $0.3$  in the normal state under 5 kOe applied field. From the plots, the susceptibility is positive and follows the typical Curie-Weiss law

$$\chi = \chi_0 + \frac{C}{T - \Theta_p} \quad (2)$$

Where  $\chi_0$  is the temperature independent susceptibility,  $C$  is the Curie constant, which is related to the effective paramagnetic moment of the ions ( $\mu_{\text{eff}}$ ), and  $\Theta_p$  is the Curie-Weiss temperature ( $\approx -98$  for  $\text{La1113}$  [6]).  $\chi^{-1}(T)$  is not linear, the slopes for both  $x=0.2$  and  $0.3$  change at around  $T \approx 145$  K. Therefore, the functions were fitted below this temperature using the equation (2) and the obtained Curie parameters are listed in Table 1. The negative value of  $\Theta_p$  for  $x=0.2$  indicates antiferromagnetic coupling between the ions in the structure. However, since La, Ca and Ba do not have a magnetic moment, decoupling should be between the  $\text{Cu}_2\text{O}$  planes and Cu-O chains in the structure. In the case of  $x=0.3$ ,  $\Theta_p$  is positive indicating the sample become paramagnetic. Note that for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $\Theta_p$  is  $\approx -20$  and increasing  $\delta$  produces the amount of oxygen in the charge reservoirs to decrease and it is reflected in the decrease of  $\Theta_p$  [19]. Similar to the irreversibility line effect above, the increase of  $\Theta_p$  could be understood from the rearrangement of the oxygen atoms in the structure after  $(\text{BO}_3)^{3-}$  inclusion. Doping  $\text{La1113}$  with  $x=0.2$  and  $0.3$  makes  $\delta$  to decrease and the amount of oxygen atoms in the charge reservoir to increase which is eventually reflected in the increase of  $\Theta_p$ . Therefore,  $\Theta_p$  is probably affected by the arrangement of oxygen atoms in the charge reservoirs rather than the total amount of them in the structure.

Table 1. Estimated physical parameters obtained after fitting the susceptibility lines in Figure 3 with the Curie-Weiss law (Equation (2)) below  $T=150$  K.

x	T <sub>c</sub> (K)	C emu K / Oe mol)	□ <sub>p</sub>	χ <sub>0</sub> (x 10 <sup>-4</sup> emu / Oe mol)	χ <sub>Pauli</sub> (x 10 <sup>-4</sup> emu/Oe mol)	m (mg)
0.2	76	0.086	-75.203	8.3229	15.10	310
0.3	73	0.0139	49.36	2.9836	7.07	430

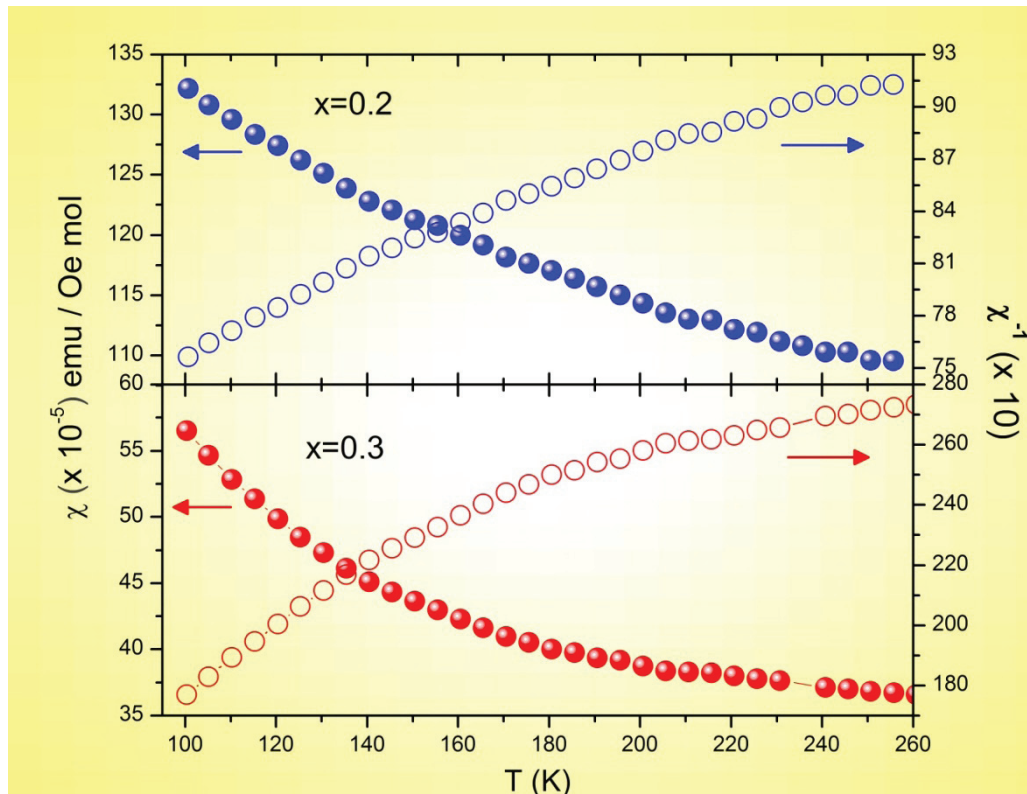


Fig. 3. Normal state susceptibility of the  $\text{LaCaBaCu}_{3-x}(\text{BO}_3)_x\text{O}_{7-\delta}$  with  $x=0, 0.2$  and  $0.3$

#### 4. Conclusions

Doping the  $\text{LaCaBaCu}_{3-x}\text{O}_7$  with  $(\text{BO}_3)^{3-}$  to obtain  $\text{LaCaBaCu}_{3-x}(\text{BO}_3)_x\text{O}_{7-\delta}$  enhances both, the irreversibility line  $H_{\text{irr}}$  and the Curie-Weiss temperature. In contrast to the stoichiometric amount of oxygen in the compound, this effect should be related with the rearrangement of them in the charge reservoirs of the crystalline structure.

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